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S.-H. Yoon, X.-S. Chai, J.Y. Zhu, J. Li, and E.W. Malcolm

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In-Digester Reduction of Organic Sulfur Compounds in Kraft Pulping

S.-H. Yoon[§], X.-S. Chai, J.Y. Zhu*, J. Li, and E. W. Malcolm
Institute of Paper Science and Technology
500 10th Street, N.W., Atlanta, GA 30318
(404) 894–5310, (404) 894–5752 (FAX), Junyong.Zhu@ipst.edu

ABSTRACT

This experimental research examines the relationship between the formation of organic sulfur compounds and delignification during kraft wood pulping. The study discovered a phase transition point (PTP) below and above which the formation of total organic sulfur compounds, with respect to delignification, changes significantly. The PTP occurs at about pulp kappa number 35 and 20 for softwoods and hardwoods, respectively. The PTP is directly related to the phase transition of kraft delignification from bulk to residual delignification. Significant in-digester odor reduction can be achieved using phase transition cooking (PTC), i.e., limiting delignification to bulk delignification phase or PTP. The study also discovered that anthraquinone (AQ) as a catalytic additive can reduce organic sulfur compound formation during kraft pulping. The reduction of sulfur compound formation is linearly proportional to the square root of the level of AQ addition (in percent). A 40% in-digester reduction in total reduced sulfur (TRS) formation can be achieved by using PTC and AQ in kraft pulping.

Keywords: Odor, Total Reduced Sulfide, Organic Sulfur Compounds, Mercaptan, Kraft Pulping, Phase Transition Cooking (PTC), Anthraquinone (AQ), Delignification.

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§ Present Address: Korea Minting and Security Printing Corporation, Buyeo Paper Mill, 17 Yeomchang-ri, Buyeo-eup, Chungnam, 323-800 Korea

* Author to whom correspondence should be addressed

INTRODUCTION

Kraft wood pulping employs white liquor, an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to remove lignin from wood. Wood chips are subjected to digestion in the white liquor at an elevated pressure and temperature (about 170°C) in a pressure vessel (digester) to release cellulosic fibers. The problem of kraft mill odor originating from the sulfide in the white liquor in the initial pulping has long been an environmental and public relations issue for the pulp and paper industry. It is caused predominantly by malodorous reduced sulfur compounds produced in the kraft pulping process, or total reduced sulfur (TRS), namely, methyl mercaptan (MM), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), and hydrogen sulfide (H_2S). MM, DMS, and DMDS are the main volatile organic sulfur compounds and are formed in the pulping process, while hydrogen sulfide is formed in the pulping chemical recovery furnaces. Although significant reduction of TRS emission has been achieved in the pulp and paper industry in the last decade with advanced odor-abatement technologies, subjective odor nuisance at very low concentrations still causes odor problems in communities surrounding a kraft mill. Furthermore, because of the enhanced sensitivity of the human nose to sulfur compounds due to the variability of odor emission from day to day, kraft mill TRS emission will always be a sensitive subject in dealing with the public and surrounding communities.

TRS formation in kraft pulping was studied as early as the 60s (Goheen, 1964; McKean et al., 1965, 1967, 1968; Douglass and Price, 1966) and 70s (Andersson, 1970). Many of these research efforts were devoted to quantification and kinetics of the organic sulfur compound formation. The general formation mechanism of the TRS has been described elsewhere (McKean et al., 1967, 1968; Andersson, 1970; and Jarvensivu et al., 1997). MM is formed

through the reaction of hydrogen sulfide ion (HS^-) with methoxyl groups (OCH_3), and DMS is formed through the reaction of mercaptide ions (CH_3S^-) and the methoxyl groups present in the pulping liquor and in lignin structure. DMDS is not formed in the pulping process, but rather through the oxidation of MM when black liquor is in contact with air (Goheen, 1964; Douglass and Price, 1966; Andersson, 1970; and Jarvensivu et al. 1997). Black liquor is spent pulping liquor named from its color; it consists mainly of wood lignin and inorganic sodium salts along with many minor volatile organic sulfur and non-sulfur species. Hydrogen sulfide is not formed under normal pulping pH conditions, but rather in the downstream processes in kraft mills where the pH of the mill streams are reduced below 10 through the dissociation of sodium sulfide (Teder, 1990; and Jarvensivu et al., 1997).

Currently, two general approaches are implemented in kraft mills to abate odor: thermal oxidation and absorption using scrubbing technologies. Thermal oxidation of TRS is achieved by two steps: collecting non-condensable gases (NCGs) in various emission vents and eliminating odorous compounds in the NCGs through combustion (Tarpey, 1995; Adam, 1994; and Wong, 1995), or incineration (Connery, 1978; Teder, 1990) to convert them into non-odorous compounds. Absorption is mainly implemented to destroy H_2S and MM in diluted NCGs through scrubbing using a spray tower or packed column (Bendig, 1995a, 1995b).

Much of the work on TRS reduction has been focused on the implementation of these technologies from the late 70s to the 90s. Significant odor reduction has been achieved. Further reduction of TRS emission using post-formation odor control technologies, e.g., oxidation, scrubbing, etc., will be very difficult and costly. Unfortunately, limited research has been conducted on developing new technologies or taking new approaches to reduce kraft mill odor. Kringstad et al. (1972) conducted in-digester oxidation (IDO) of kraft black liquor using oxygen.

They found that both MM and DMS can be reduced with the application of a large amount of oxygen into the pulping liquor. Tormund and Teder (1987) found that significant amounts of MM and DMS formed during pulping can be converted to non-volatile compounds by reaction with polysulfide or polythionate immediately before releasing the pulp from the digester (a post-formation in-digester reduction approach). Neither of these two technologies has been implemented in kraft mills.

All the work dealing with kraft mill odor discussed above was focused only on the environmental aspect of the problem, i.e., understanding odor formation kinetics and mechanisms and adopting post-formation odor reduction technologies. In this study, we took an integrated approach, i.e., to examine the relation of odor formation (an environmental issue) with delignification (a production and product-quality issue). We found that odorous compounds can be significantly reduced before formation with an understanding of the relationship between odor formation and delignification. We propose an In-Digester Odor Reduction (IDOR) methodology based on the understanding of that relationship, a novel and economical way to significantly reduce kraft mill odor and to further improve the air quality, the environment, and public relations with the surrounding communities.

EXPERIMENTAL

Kraft Pulping

Kraft pulping experiments were conducted using 8 rotating bomb digesters (cylindrical high pressure vessels mounted on a rotating device) in an oil bath. The volume of the digester is 500 mL. The rotating speed of the digesters was 6 rpm. Four different softwood species, including Douglas-fir, white spruce, western hemlock, and loblolly pine, and six hardwood

species, including aspen, bass, birch, maple, oak, and sweet gum, were used in the experiments. 50 grams (ODW) of wood chips in each digester were subjected to a conventional kraft pulping in which the wood chips are cooked with the white liquor while the cooking temperature is linearly ramped to a desired terminal temperature and maintained for certain time. In the pulping of southern pine, a pulping liquor-to-wood ratio of 4, an 18% active alkali (AA) charge (the amount of the sum of sodium sulfide and sodium hydroxide as of Na_2O divided by the oven-dry mass of the wood chips), and four AQ catalyst concentrations of 0, 0.025, 0.05, and 0.1% were used. For the pulping of the rest of the wood species, the pulping liquor-to-wood ratio was 3.7, sulfidity was 31%, and the active alkali charge was 17% for softwoods and 16% for all hardwoods. In the kraft pulping of southern pine and maple, three sulfidity levels of 10, 20, and 30% were used; sulfidity is the amount of sodium sulfide divided by the amount of the sum of sodium sulfide and sodium hydroxide. Cooking temperature was ramped from a room temperature of 23°C to 170°C in 70 minutes or at a rate of 2.1°C per minute. Cooking times at the preset maximum temperature of 170°C were varied to study the time-dependent formation of organic sulfide compounds in pulping. Each bomb was quenched in an ice bath immediately after the completion of the cook. Pulps obtained from each cook were disintegrated in a blender and thoroughly washed on a 200-mesh screen with cold (tap) water. Thick pulp pads were prepared and air-dried for the measurement of pulp yields and kappa numbers using TAPPI standard methods. Black liquor samples collected from each digester were analyzed to determine the chemical strength of the spent cooking liquor, i.e., effective alkali charge (the hydroxide ion concentration) and sulfidity, and the TRS concentrations, i.e., MM, DMS, and DMDS. H_2S was not formed in pulping due to high pH.

TRS Analysis

Accurate determination of organic sulfide compounds in kraft pulping spent liquors is the key to the present research. Unfortunately, a limited number of methods are available for the analysis of sulfur compounds in pulping spent liquors. The most commonly used solvent extraction technique (Andersson and Bergstrom, 1969; and Prakash, 1976) is not only tedious and time-consuming but also gradually becoming outdated because many high-extraction-efficiency solvents, e.g., carbon tetrachloride, are being prohibited for laboratory usage due to environmental regulations. In this study, the full-evaporation headspace gas chromatographic (FE-HSGC) method that we developed in a previous study (Chai et al., 2000) was employed. The FE-HSGC method is based on the principle of near-complete analyte transfer from the liquid phase into the vapor phase when a very small sample is heated in a sample vial; therefore, the analyte in the liquid phase can be analyzed by direct headspace gas chromatography without sample pretreatment requirements. It is simple, rapid, and accurate as demonstrated in our published study (Chai et al., 2000).

The measurement apparatus consisted of an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.) and a pulsed flame photometric detector (Cheskis et al., 1993; Amirav and Jing, 1995) (PFPD, O.I. Analytical, TX, U.S.A.). GC conditions were: HP-5 capillary column at 30°C and carrier gas helium flow rate of 1.1 mL/min. The PFPD was run with hydrogen and airflow rates (the system requires two airflows) of 11.5, 10, and 15 mL/min, respectively. The PFPD has the unique characteristic of high selectivity of sulfur compounds over hydrocarbons (10^5:1), which is very suitable for analysis of organic sulfur compounds in a mixture containing a high amount of hydrocarbons, such as black liquor. Headspace operating conditions were: 5 min. strong shaking

for equilibration of the sample, vial pressurization time of 0.2 min, sample loop fill time of 1.0 min, and loop equilibration time of 0.05 min. The sample vials were purged by nitrogen to minimize the oxidation of MM to obtain accurate MM analysis. The sample preparation and measurement procedures were as follows: inject 10 μL of sample solution into a closed 21.6-mL vial by micro-syringe and place it in the headspace sample tray for HS-GC measurements. For quantifying total MM, 50 μL of 0.5 M sulfuric acid was added to the vial for the acidification of the black liquor to convert mercaptide ions to MM; due to high alkalinity only mercaptide ions are present in black liquors.

RESULTS AND DISCUSSIONS

Data Reproducibility

The repeatability of the analytical method used in the present experiments was reported in our previous study (Chai et al., 2000). We added 1 μg of DMS to 12 μL of soda black liquor. Soda black liquors derived from a sulfur-free soda pulping process have a similar sample matrix to that of kraft black liquor, but do not contain any sulfur compounds. It was found that the relative standard deviation of the square root of the signal intensity (proportional to the DMS mass) is only 2%, indicating excellent repeatability of the analytical method. The repeatability of MM is expected to be poorer than that of DMS mainly due to acidification and oxidation problems. MM can be easily be oxidized by a very small amount of oxygen. To demonstrate the reproducibility of the present experiments, we conducted two separate sets of kraft pulping experiments using loblolly pine under sulfidity of 30% and active alkali 18%. Each set of experiments were prepared and conducted in the same day. But the two sets of experiments were conducted about 3 months apart. The measured MM and DMS formation along with the pulp

kappa number are shown in Fig.1. The results indicate that the measured DMS and MM formation and the pulp kappa numbers in the two sets of experiments agree very well in trends but with some systematic discrepancies. For example, experiment I showed higher DMS and MM formation and lower kappa number. We believe this consistency discrepancy is mainly due to the systematic difference between the two sets of pulping experiments. There are many systematic variables that could contribute to this difference, such as, the variability of wood chips (dimension, quality, uniformity, etc.), the deviations of the pulping temperature due imperfect temperature control, the systematic errors in black liquor sampling due to oxidation, or even the variation in the application of pulping chemicals. Considering the many variables and the 3-month time delay between the two sets of experiments, the reproducibility of the data is reasonably good.

Time-Dependent Organic Sulfur Compound Formation

Figure 2 shows the time-dependent formation of organic sulfur compounds, namely MM and DMS, in a set of conventional kraft pulping processes of southern pine. The sulfidity was 30%. DMDS was not found in the spent pulping liquor, which agrees with the conclusions reported by Goheen (1964), McKean et al. (1965), Douglas and Price (1966), and Andersson (1970). The time-dependent data show that the formation of MM and DMS was slow at the beginning of the pulping process, but increased exponentially (formation rate transition) as the pulping process continued. The formation rate transition point (FRTP) occurs right as the pulping temperature reaches 170°C (the 4^{th} data point corresponding to a pulping time of 70 min.). The formation of MM is much earlier than that of DMS. Figure 2 also shows that the present data agree in general with those obtained by Andersson (1970). The discrepancy at the early stage of the pulping is due to the difference in the cooking temperature profiles, as shown.

Because Andersson (1970) used a sulfidity of 33%, higher than the 30% used in the present work, a little more MM was formed in his study.

The time-dependent volatile organic sulfur compound formation data provide detailed information about the formation kinetics and have been well documented in the literature (Goheen, 1964; McKean et al., 1965, 1967; Douglass and Price, 1966; Andersson, 1970). The data clearly show that the formation of organic sulfur compounds goes through a slow stage at the beginning of the pulping and a rapid increase stage after the cooking temperature reaches 170°C. However, the data did not provide any information about the degree of delignification corresponding to a quantified formation of organic sulfur compounds. Research on the correlation between the formation of organic sulfur compounds and delignification has not been reported in the literature. It will be very interesting and beneficial to correlate organic sulfur compound formation to delignification. This integrated approach, adopted in the present study, leads to the discovery of phase transition cooking (PTC) methodology for in-digester odor reduction (IDOR) at its source (before formation).

Phase Transition Cooking (PTC) for In-Digester Odor Reduction

To relate the formation of organic sulfur compounds to delignification, we determined the kappa number of each pulp sample for data presented in the present study . Kappa number is a parameter that measures the reactivity of the total residual lignin in the pulp; a high kappa means less delignification for a given pulp or wood species. Figure 3 shows the correlation of sulfur compound formation to the kappa number for a set of kraft conventional pulping processes of southern pine. The corresponding time-dependent formation data are presented in Fig. 2. The results demonstrate that initially the formation of organic sulfur compounds linearly increases with the reduction of kappa number. Further reduction of kappa number as delignification

continues results in a rapid increase of the formation of sulfur compounds. The transition point occurs at about a kappa number of 35 (between the 6^{th} and 7^{th} data points corresponding to a pulping time of 120 min.). We call this the phase transition point (PTP) based on the assumption that the pulping process enters residue delignification from the bulk delignification phase. The PTP differs from the formation rate transition point (FRTP) in terms of the corresponding pulping time, kappa number, physical meaning, and practical importance. The FRTP (at 70 min. in the pulping process) has no practical importance because it is derived from the time-dependent measurement with no relation to delignification. Furthermore, the kappa number corresponding to the FRTP is about 140; actually, kappa number is not a good measure at the beginning of the pulping process. The wood chips essentially have not yet been pulped or only about 50% of the wood lignin has been removed through pulping. However, the kappa number at PTP has been reduced to about 35 for conventional kraft pulping of southern pine, meaning a significant amount of lignin (bulk lignin) has been removed. Therefore, PTP has significant importance in mill practice.

The integrated approach of studying environmental impact with production optimization led us to examine the relationship between the formation of sulfur compounds and delignification. It is well known that kappa number reduces rapidly in the early stage of bulk delignification. This rapid lignin-removal process cannot be sustained in any chemical pulping processes; therefore, further cooking in the later stage of residual delignification only results in a slight kappa reduction. Figure 4 demonstrates this characteristic of delignification with a kraft pulping of southern pine where the transition from bulk to residual delignification occurs at a kappa number around 35 (exactly the same kappa at PTP). To obtain a fixed kappa reduction, one would have to cook longer or use more energy once the delignification enters the residual

phase (kappa < 35 for southern pine), which results in more formation of organic sulfur compounds (even though their formation rates remain unchanged as shown in Fig. 2). We propose PTP pulping to achieve in-digester odor reduction (IDOR), i.e., to cook southern pine to PTP or a kappa number of 35 to remove the bulk lignin significantly reduce the formation of organic sulfur compounds and mill odor. Furthermore, we propose to use other processes that do not produce odor, such as oxygen delignification, to remove the residue lignin and achieve the required level of delignification (kappa number around 28 for a bleachable grade of softwood pulp).

To demonstrate that the PTP pulping concept is universally valid, we conducted conventional kraft pulping of 4 softwoods and 6 hardwoods. Figure 5 shows the formation of total reduced sulfur compounds, i.e., MM plus DMS, in relation to delignification pulp kappa number. The sulfidity was 30% for southern pine and maple and 31% for the rest of the wood species, as stated in the experimental section. The results indicate that kraft pulping of softwoods produces a greater amount of organic sulfur compounds than that of hardwoods at the same kappa number (the kappa numbers are different for an equivalent grade of softwood and hardwood pulp). The results also show that the total organic sulfur compounds formed from pulping of all softwoods fall into one single curve and the sulfur compound data from all hardwood pulping fall into another single curve, regardless of the specific wood species within the general categorization of hardwood and softwood. Furthermore, the slopes of the two TRS formation curves show an abrupt change at a critical kappa number, respectively, meaning that a PTP exists in both hardwood and softwood pulping. The kappa number at the PTP is 35 for softwoods and 20 for hardwoods. When kraft cooking is terminated around the critical point for the purpose of odor reduction, we refer to it as the phase transition cooking (PTC). It is our

understanding that the transition point is directly related to the phase transition of kraft delignification from bulk delignification to residual delignification as demonstrated in Fig. 4, where the kappa number reduction rate underwent an abrupt change at a kappa number of 35 for southern pine (softwood). Thus, when the different sulfidities and cooking processes are used, the actual kappa number of the transition may be different.

The data in Fig. 5 indicate that the total organic sulfur compounds formed during the post-PTP cooking stage are 30% and 25%, respectively, for bleachable grade hardwood pulping with a final kappa number of 14 and bleachable grade softwood with a final kappa number of 28. Therefore, it is feasible to significantly reduce TRS formation in kraft pulping by limiting the degree of delignification to the PTP at which the pulp kappa number is 20 and 35 for hardwoods and softwoods, respectively. The increased amount of lignin residue can be removed through other means, such as oxygen delignification, in which odor compounds will not be formed because sulfur compounds are not used.

Catalyst Anthraquinone (AQ) Addition

AQ has been well known to possess a marked capability of accelerating the delignification while at the same time stabilizing the carbohydrates toward alkaline degradation in the alkaline pulping process (Sjostrom, 1993). During pulping, AQ is reduced to anthrahydroquinone (AHQ) by carbohydrate-reducing end groups, which, in turn, are oxidized to alkali-stable aldonic acid groups. The AHQ now acts as an effective nucleophile with regard to the lignin $\beta - O - 4$ linkages and is simultaneously oxidized to AQ. As a result of this reduction-oxidation cycle, AQ could have a significant effect on delignification as well as gains in pulp yield. From the reaction kinetics, one can easily find that catalyst AQ does not affect organic sulfur compound formation, which is verified in the present study. As shown in Fig. 6,

the TRS formation rate does not change with the addition of 0.05% of AQ in kraft pulping of southern pine and maple. Only when we correlate TRS formation with delignification have we discovered that AQ can change the correlation between the formation of organic sulfur compounds and delignification due to improved delignification. Therefore, we believe that TRS formation can be reduced by using a reduced pulping time with AQ to achieve an equivalent delignification (or kappa number). Significant reduction in TRS formation with AQ addition in kraft pulping of southern pine and maple was shown in Figs. 7 and 8 over a wide range of sulfidity variations from 10 to 30%. Even in such a wide sulfidity range, the PTP remains the same, i.e., 20 and 35, for maple and southern pine, respectively.

To further demonstrate the effect of AQ addition on TRS formation reduction, we varied the level of AQ addition in pulping. We found that the TRS formation decreases linearly with the square root of the AQ (in percent) added in kraft pulping of southern pine, as shown in Fig. 9. We found that TRS formation can be reduced by 20 and 30% with the addition of 0.05% AQ in the kraft pulping of southern pine to kappa numbers of 30 and 40, respectively. The difference in the percent of reduction of TRS formation between kappa number 30 and 40, may be due to the fact that the PTP is at a kappa number of 35, indicating that the addition of AQ is perhaps more effective to the bulk delignification phase of pulping.

Combined Effects of Pre-PTP Cooking and AQ Addition

From the results shown above, it can be strongly postulated that by using both pre-PTP cooking and AQ addition, TRS emission from the kraft digester can be reduced approximately 40%.

CONCLUSION

We conducted the first experimental study to investigate the relationship between the formation of organic sulfur compounds and delignification in kraft pulping. The results show that the formation of organic sulfur compounds increases as delignification proceeds. Further removal of lignin results in a rapid increase in the formation of sulfur compounds. The transition point occurs at about a kappa number of 35 and 20 for softwoods and hardwoods, respectively. Furthermore, all the softwoods and hardwoods have the same relationship between formation of sulfur compounds and delignification. Therefore, the transition point is directly related to the phase transition of kraft delignification from bulk delignification to residual delignification. We define this transition point as phase transition point (PTP). When kraft cooking is terminated around the critical point for the purpose of odor reduction, we define it as the phase transition cooking (PTC). The results also indicate that anthraquinone (AQ) as a catalytic additive can be used for the purpose of TRS reduction during kraft digestion. The reduction of sulfur compound formation is linearly proportional to the square root of the level of AQ addition (in percent). Based on data obtained, we found that it is possible to reduce TRS formation by 40% during kraft pulping simply by combining the following two methods: limiting the degree of delignification to the bulk delignification phase (using PTC) and using AQ as a catalytic additive in kraft pulping.

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List of Figures

Fig. 1

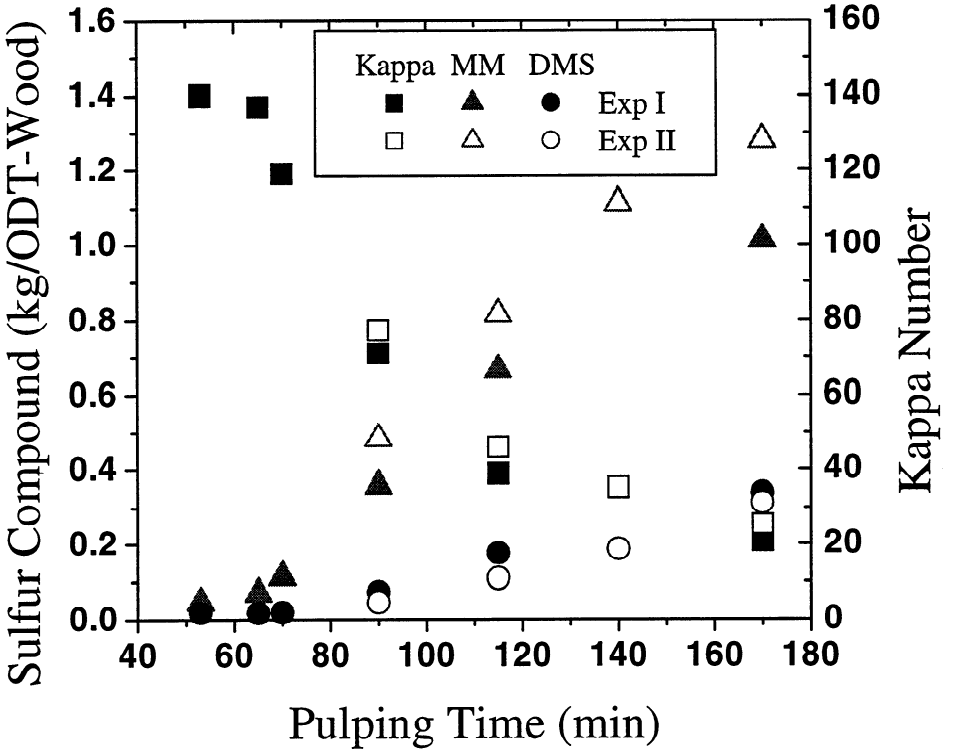

Kappa MM DMS
Exp I
Exp II
Sulfur Compound (kg/ODT-Wood)
Kappa Number
Pulping Time (min)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
160
140
120
100
80
60
40
20
0
40
60
80
100
120
140
160
180

Fig. 2

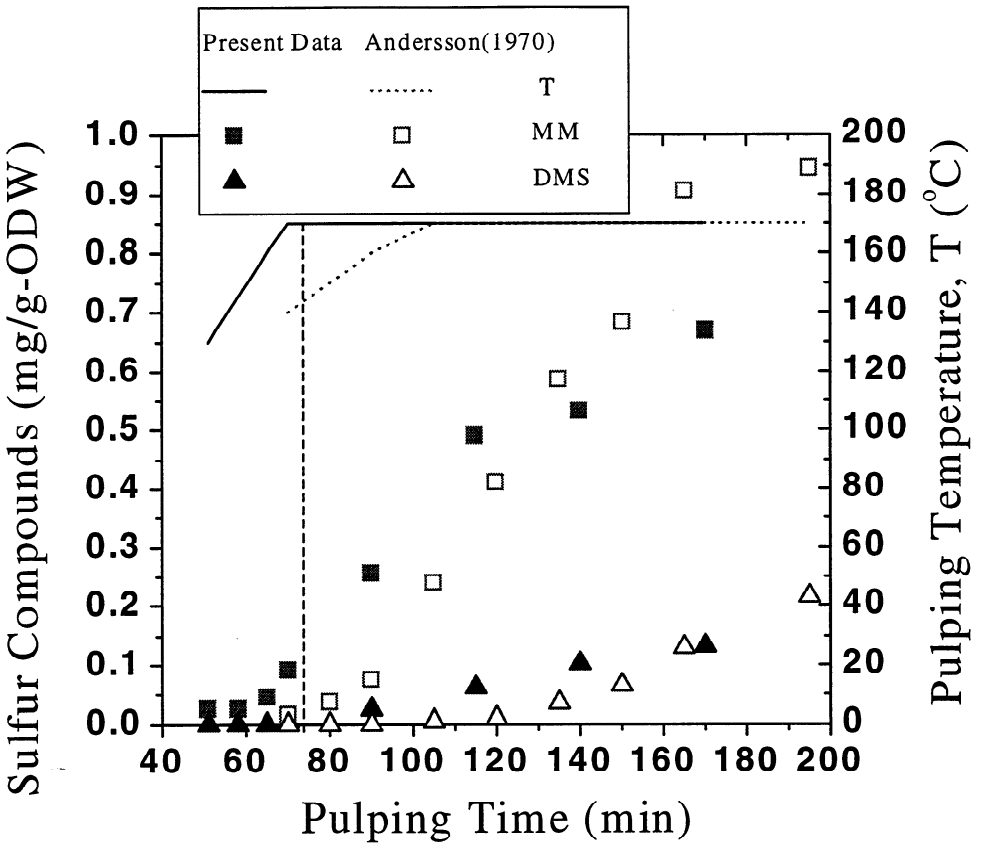

Present Data
Andersson(1970)
T
MM
DMS
Sulfur Compounds (mg/g-ODW)
Pulping Temperature, T (°C)
Pulping Time (min)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
200
180
160
140
120
100
80
60
40
20
0
40 60 80 100 120 140 160 180 200

Fig. 3

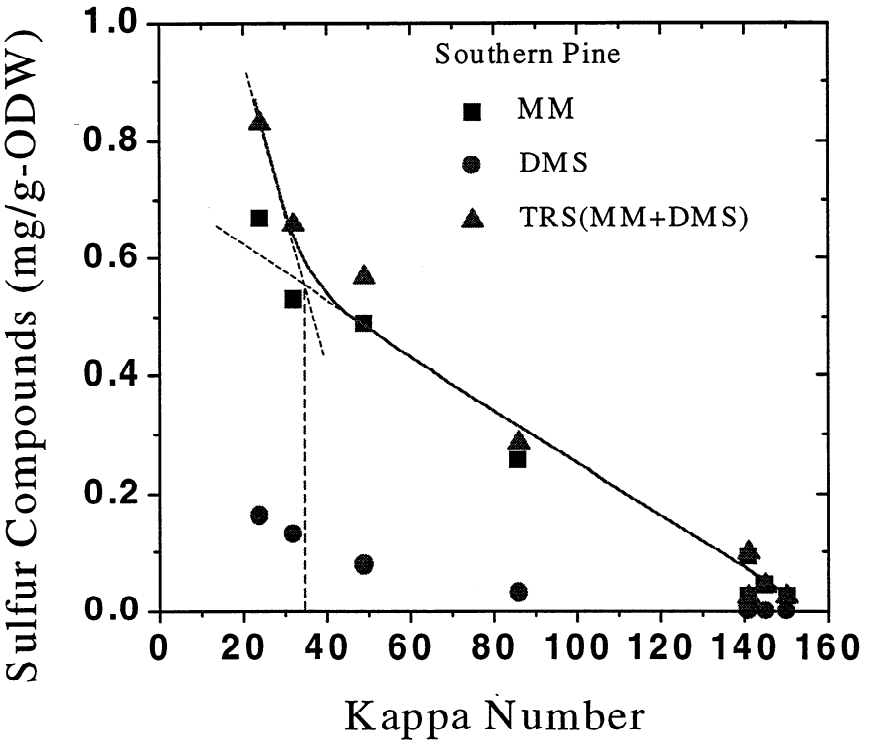

Southern Pine
MM
DMS
TRS(MM+DMS)
Sulfur Compounds (mg/g-ODW)
Kappa Number
1.0
0.8
0.6
0.4
0.2
0.0
0 20 40 60 80 100 120 140 160

Fig. 4

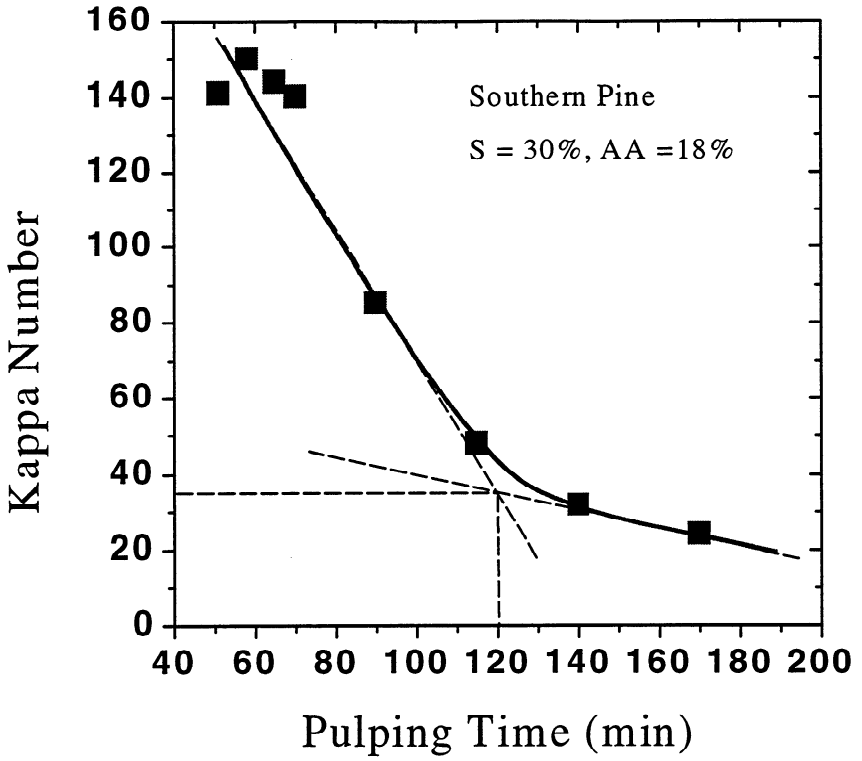

Southern Pine
S = 30%, AA =18%
Kappa Number
Pulping Time (min)
160
140
120
100
80
60
40
20
0
40 60 80 100 120 140 160 180 200

Fig. 5

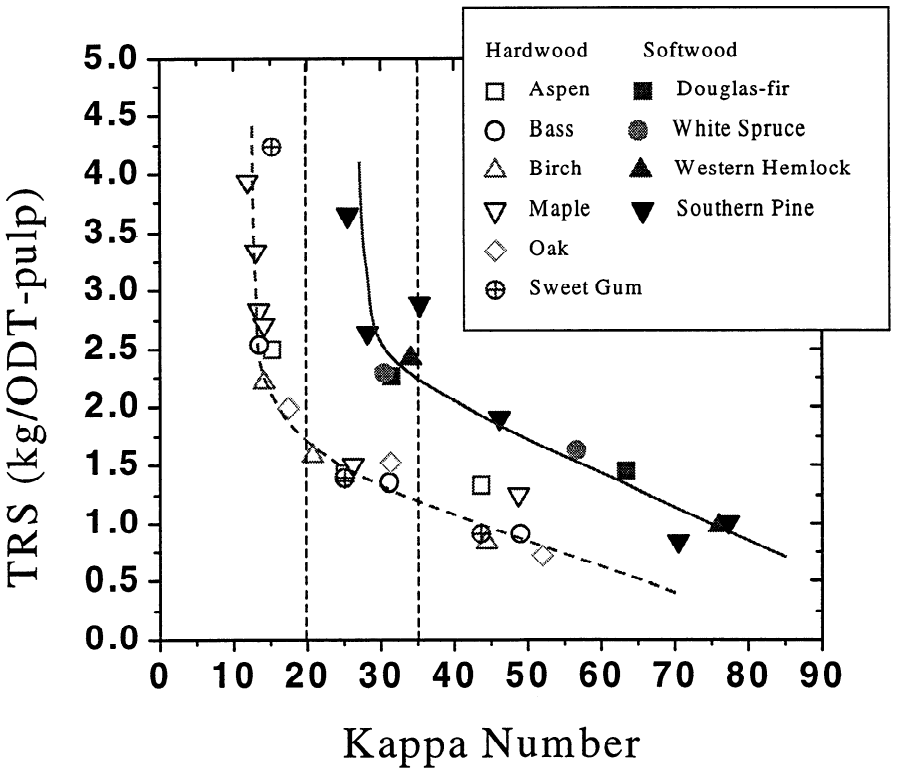

Hardwood
Softwood
Aspen
Bass
Birch
Maple
Oak
Sweet Gum
Douglas-fir
White Spruce
Western Hemlock
Southern Pine
TRS (kg/ODT-pulp)
Kappa Number
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0 10 20 30 40 50 60 70 80 90

Fig. 6

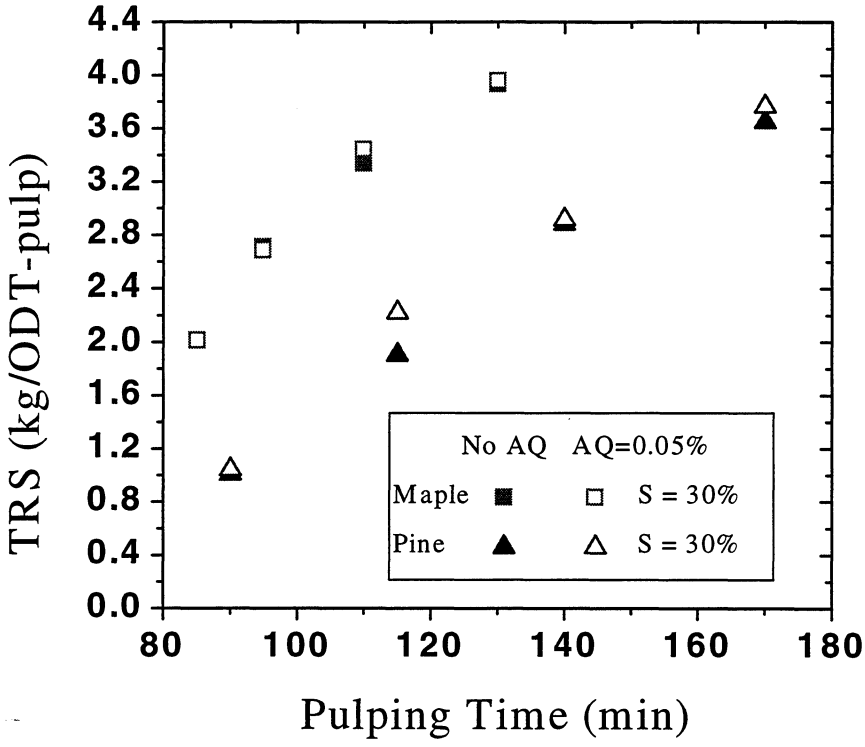

TRS (kg/ODT-pulp)
Pulping Time (min)
No AQ AQ=0.05%
Maple S = 30%
Pine S = 30%

Fig. 7

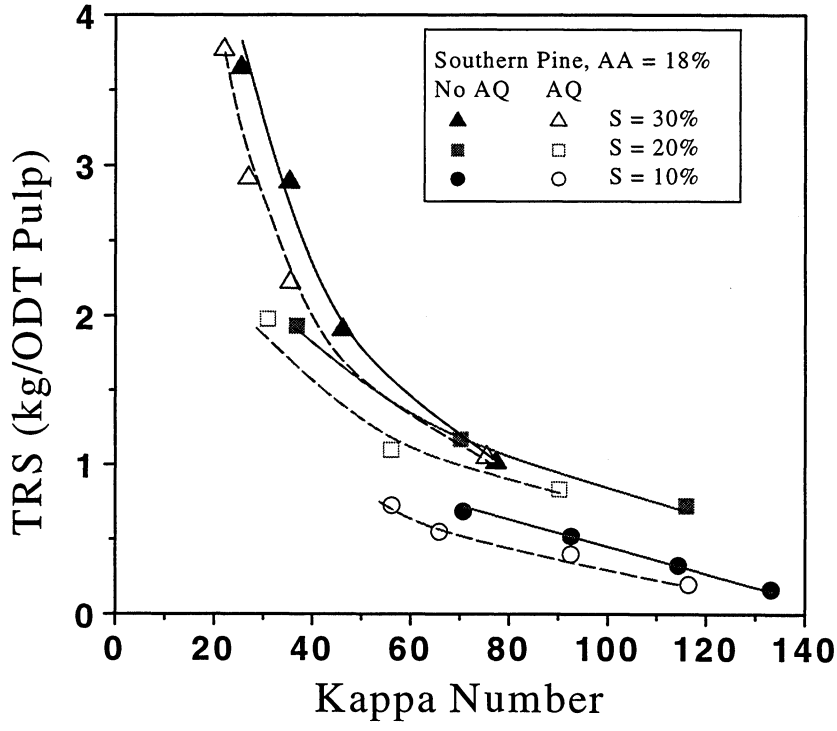

TRS (kg/ODT Pulp)
Kappa Number
Southern Pine, AA = 18%
No AQ AQ
S = 30%
S = 20%
S = 10%

Fig. 8

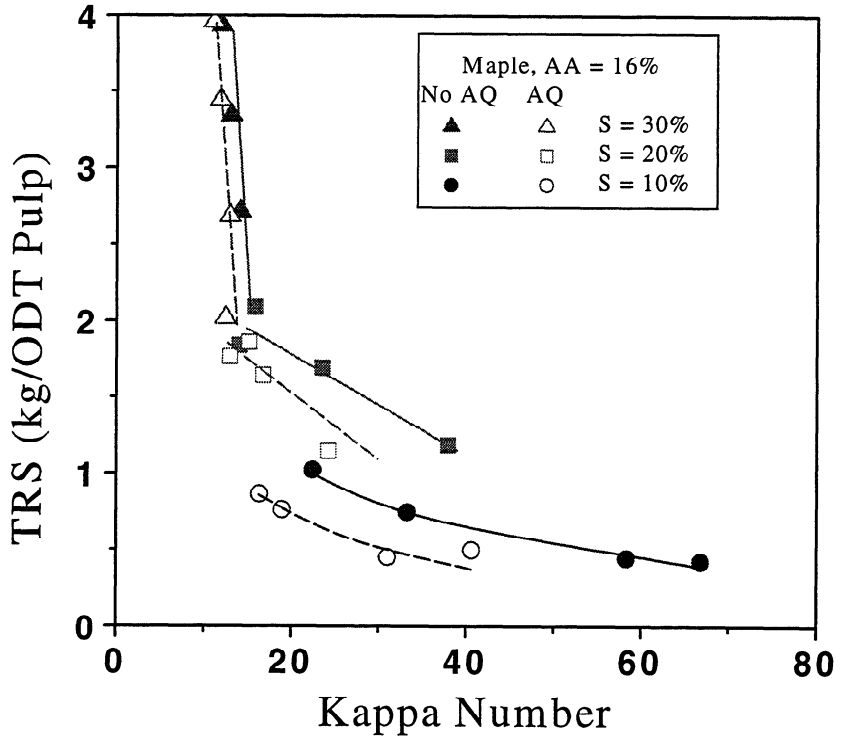
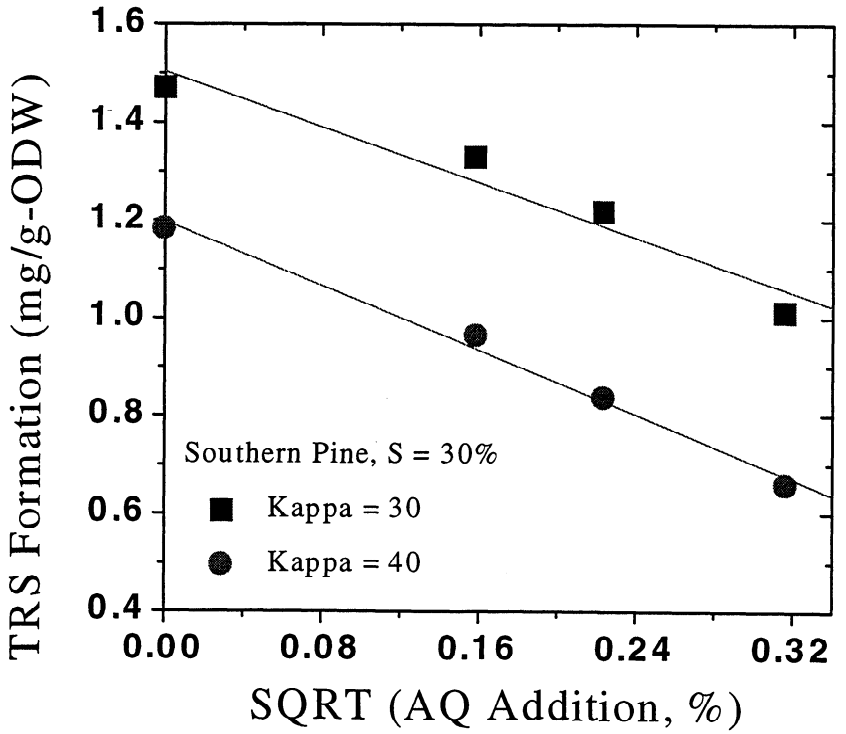

Maple, AA = 16%
No AQ AQ
S = 30%
S = 20%
S = 10%
TRS (kg/ODT Pulp)
Kappa Number
0
1
2
3
4
0
20
40
60
80

Fig. 9


Southern Pine, S = 30%
Kappa = 30
Kappa = 40
TRS Formation (mg/g-ODW)
SQRT (AQ Addition, %)
0.4
0.6
0.8
1.0
1.2
1.4
1.6
0.00
0.08
0.16
0.24
0.32